



W099/41322

DESCRIPTION

COATING MATERIAL FOR FORMING PHOTOCATALYTIC HYDROPHILIC FILM, METHOD OF FORMING PHOTOCATALYTIC HYDROPHILIC FILM, AND PHOTOCATALYTIC HYDROPHILIC MEMBER

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a technique for forming a photocatalytic hydrophilic film. More particularly, the present invention relates to a coating material capable of forming a photocatalytic hydrophilic film, a method of forming a photocatalytic hydrophilic film using the coating material, and to a photocatalytic hydrophilic member obtained using the same.

Background Art

PCT/WO96/29375 discloses that the surface of a photocatalyst-containing layer formed on the surface of a substrate exhibits a high degree of hydrophilicity (e.g. 10° or less in terms of the contact angle with water) upon photoexcitation of photocatalyst. The above document discloses properties of the photocatalyst can be used to improve the anti-fogging effect and the visibility-securing properties of transparent members such as glass, lens, and mirrors, and to improve water or rain detergency of the surface of an article.

Functional materials utilizing the function of the photocatalyst have been manufactured by preparing a coating liquid containing a photocatalyst or its precursor, applying the coating liquid to a substrate, and drying or sintering the applied liquid. For example, the above-mentioned functional materials are manufactured by applying a titania sol formed from a titanium alkoxide and an alcohol amine or a sol prepared by dissolving particles such as TiO_2 , ZnO , or SrTiO_3 in a water-based solvent to the

substrate surface, and drying or sintering the applied liquid. Specific methods include a method in which a titanium alkoxide, a TiO_2 sol, a combination of a TiO_2 sol and an SiO_2 sol, a combination of a TiO_2 sol and a bifunctional silicone, or a combination of a TiO_2 sol and a trifunctional silicone is used as the starting material.

JP-A-9-248467 discloses a method using a titanium alkoxide and a TiO_2 sol in combination. A photocatalytic hydrophilic film is generally required to have a high degree of hydrophilicity. In addition, the photocatalytic hydrophilic film must have excellent durability, hardness, transparency, and high visible light transmittance.

To the best knowledge of the inventors, using a mixture of an amorphous titania precursor, crystalline titania, and a precursor which can be converted to a compound having a siloxane bond as a coating material has not yet been proposed.

SUMMARY OF THE INVENTION

The inventors have recently found that a hydrophilic film exhibits satisfactory durability, hardness, transparency, and visible light transmittance and retains hydrophilicity for a long time even when shaded from light can be obtained using a coating material comprising at least an amorphous titania precursor, crystalline titania, and a precursor which can be converted to a compound having a siloxane bond. The present invention has been made based on this finding.

Accordingly, an object of the present invention is to provide a coating material capable of forming a photocatalytic hydrophilic film which exhibits excellent in durability, transparency, and visible light transmittance and retains hydrophilicity for a long time even when shaded from light.

A coating material for forming a photocatalytic hydrophilic film according to the present invention comprises at least an amorphous titania precursor, crystalline titania, and a precursor which can be converted to a compound having a siloxane bond.

DETAILED DESCRIPTION OF THE INVENTION

Coating material

A hydrophilic film prepared using the coating material according to the present invention exhibits excellent durability, hardness, and visible light transmittance. In particular, the film obtained by the coating material according to the present invention exhibits excellent durability. Specifically, the film retains hydrophilicity for a long time when evaluated using an accelerated outdoor weatherability test called a sunshine weather meter (SWM) test.

The coating material for forming a photocatalytic hydrophilic film according to the present invention basically contains an amorphous titania precursor, crystalline titania, and a precursor which can be converted to a compound having a siloxane bond.

The amorphous titania precursor such as a titanium alkoxide is crystallized by heat treatment to form a titanium oxide. It is considered that the titanium oxide not only exhibits photocatalytic hydrophilizing capability but forms a film with improved density and strength by incorporating crystalline titania. The crystalline titania realizes photocatalytic hydrophilizing capability which is stable and can be retained for a long time. The precursor which can be converted to a compound having a siloxane bond forms an amorphous silica by heat treatment or the like. The silica serves to retain the hydrophilicity of titanium oxide for a long time even when shaded from light. In addition, it is reported that the precursor which can be converted to a compound having a siloxane bond may produce a highly uniform Ti-O-Si bond when heated simultaneously with the amorphous titania precursor. As a result, crystallization of TiO_2 is suppressed, and the hydrophilizing capability of the photocatalyst cannot be fully exhibited by photoexcitation (Preparation of Catalyst Using Metal Alkoxide, IPC (1993), page 337). However, the coating material according to the present invention can provide an excellent film without causing the above-mentioned problem. Due to the presence of the precursor which can be converted to a compound having a siloxane

bond, a film obtained by the coating material according to the present invention is superior to a film obtained using a coating material comprising an amorphous titania precursor and crystalline titania in abrasion resistance and capability of retaining hydrophilicity for a long time even when shaded from light. A film obtained by the coating material according to the present invention is superior to a film obtained using a coating material comprising an amorphous titania precursor, crystalline titania, and a crystalline silica in abrasion resistance.

(a) Crystalline titania

The crystalline titania used in the present invention may be of an anatase type, rutile type, or brookite type crystal system. In the present invention, it is preferred that the crystalline titania be added to the coating material as a stable system without precipitating in a solution. In this respect, a TiO_2 sol prepared by suspending and dispersing fine titania particles in a solvent is preferable. This type of sol is readily obtained on the market.

According to a preferred aspect of the present invention, the average particle diameter of the TiO_2 sol is preferably 50 nm or less, more preferably around 5 to 10 nm. Use of a sol having such an average particle diameter enables the crystalline titania to be dispersed stably in the coating material, and has such an advantage that the visible light transmittance of the film is improved.

According to another preferred aspect of the present invention, using a TiO_2 sol having a broader particle diameter distribution or having a plurality of average diameter peaks is advantageous in respect of forming a film with abrasion resistance.

The average particle diameter of the sol may be determined by X-ray diffractometry.

(b) Amorphous titania precursor

In the present invention, the term “amorphous titania precursor” refers to a precursor capable of forming a crystalline titania by heating. Specific examples

include organic titanium compounds such as an alkoxide, a chelate, and an acetate of titanium; and inorganic titanium compounds such as TiCl_4 and $\text{Ti}(\text{SO}_4)_2$. Examples of the titanium alkoxide include tetraethoxytitanium, tetraisopropoxytitanium, tetra-n-propoxytitanium, tetrabutoxytitanium, and tetramethoxytitanium. A (partial) hydrolyzate may be obtained by adding a titanium alkoxide, a hydrolysis retardant such as hydrochloric acid or ethylamine, diluting with alcohol such as ethanol and propanol, and partially or completely hydrolyzing the resulting mixture. The resulting (partial) hydrolyzate can be used as the amorphous titania precursor in the present invention.

According to a preferred aspect of the present invention, the amount of the crystalline titania accounts for preferably 6 wt% or more, and more preferably from 8 wt% to 45 wt% of the total amount of the titanium oxide. According to still another aspect of the present invention, the crystalline titania content accounts for 6 wt% or more and 40 wt% or less of the total solid content of the coating material.

(c) Precursor which can be converted to a compound having a siloxane bond

In the present invention, the term “precursor which can be converted to a compound having a siloxane bond” preferably refers to a precursor capable of forming an amorphous silica or silicone as a result of film formation. According to the present invention, the term “film formation” of the precursor refers to a state where an amorphous silica or silicone film is formed by hydrolysis, condensation polymerization, or the like by heating or by the action of a catalyst. In addition, the “film formation” of the precursor refers to a state where an amorphous silica or silicone film is formed by applying a coating material containing the precursor to a substrate and removing the solvent component.

According to a preferred aspect of the present invention, preferred examples of the precursor which can be converted to a compound having a siloxane bond include a silica precursor which can form an amorphous silica by heating, its hydrolyzate, its partial hydrolyzate, its hydrolysis-polycondensation product, its partial

hydrolysis-polycondensation product, a mixture thereof. As specific examples of the silica precursor which can form an amorphous silica by heating, hydrolyzable silane derivatives expressed by the following general formula can be given.



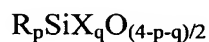
wherein R represents one or more members selected from the group consisting of a hydrogen atom and an organic group, X represents one or more members selected from the group consisting of an alkoxy group and a halogen atom, and p represents 1 or 2.

The organic group represented by R refers to an alkyl group (preferably, an unsubstituted alkyl group having 1 to 18 carbon atoms, and most preferably an alkyl group having 3 to 18 carbon atoms) or an aryl group (preferably phenyl). Preferred specific examples of the hydrolyzable silanes derivative include methyltrimethoxysilane, methyltriethoxysilane, methyltripropoxysilane, methyltributoxysilane, ethyltrimethoxysilane, ethyltriethoxysilane, ethyltripropoxysilane, ethyltributoxysilane, phenyltrimethoxysilane, phenyltriethoxysilane, phenyltripropoxysilane, phenyltributoxysilane, dimethyldimethoxysilane, dimethyldiethoxysilane, dimethyldipropoxysilane, dimethyldibutoxysilane, diethyldimethoxysilane, diethyldiethoxysilane, diethyldipropoxysilane, diethyldibutoxysilane, phenylmethyldimethoxysilane, phenylmethyldiethoxysilane, phenylmethyldipropoxysilane, phenylmethyldibutoxysilane, n-propyltrimethoxysilane, n-propyltriethoxysilane, n-propyltripropoxysilane, n-propyltributoxysilane, gamma-glycidoxypropyltrimethoxysilane, gamma-methacryloxypropyltrimethoxysilane, 3-chloropropyltrimethoxysilane, octadecyltriethoxysilane, vinyltriethoxysilane, gamma-aminopropyltrimethoxysilane, N-beta(aminoethyl)gamma-aminopropyltrimethoxysilane, gamma-mercaptopropyltrimethoxysilane, and beta-(3,4-epoxycyclohexyl)ethyltrimethoxysilane.

Other preferred examples of the silica precursor which can form an amorphous

silica by heating according to the present invention includes a precursor prepared by partial hydrolysis and dehydration-polycondensation of the above-mentioned hydrolyzable silane derivative and a precursor prepared by dehydration-polycondensation of a partial hydrolyzate of the above-mentioned hydrolyzable silane derivative and a partial hydrolyzate of tetramethoxysilane, tetraethoxysilane, tetrabutoxysilane, tetrapropoxysilane, tetrabutoxysilane, or diethoxydimethoxysilane.

A siloxane obtained by the above partial hydrolysis and dehydration-polycondensation is expressed by the following average compositional formula:



wherein R is as defined above, X represents one or more members selected from the group consisting of an alkoxy group and a halogen atom, p represents a number satisfying $0 < p < 2$, and q represents a number satisfying $0 < q < 4$.

Other preferred examples of the silica precursor which can form an amorphous silica by heating according to the present invention include tetrafunctional hydrolyzable silane derivatives expressed by the following general formula:



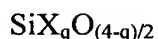
wherein X represents one or more members selected from the group consisting of an alkoxy group and a halogen atom.

As preferred specific examples of the above tetrafunctional hydrolyzable silane derivatives, tetramethoxysilane, tetraethoxysilane, tetrapropoxysilane, tetrabutoxysilane, diethoxydimethoxysilane, tetrachlorosilane, tetrabromosilane, silanol, and dimethoxydiethoxysilane can be given.

Other preferred examples of the silica precursor which can form an amorphous silica by heating according to the present invention include a product obtained by hydrolysis and dehydration-polycondensation of the above-described tetrafunctional

hydrolyzable silane derivative and a product obtained by partial hydrolysis and dehydration-polycondensation polymerization of the above-described tetrafunctional hydrolyzable silane derivative.

A silicate obtained by the above partial hydrolysis and dehydration-polycondensation is expressed by the following average compositional formula:



wherein X represents one or more members selected from the group consisting of an alkoxy group and a halogen atom, and q is a number satisfying $0 < q < 4$.

According to a preferred aspect of the present invention, the converted weight of SiO_2 in the precursor which can be converted to a compound having a siloxane bond preferably 50% or less of the converted weight of TiO_2 in the above-mentioned amorphous titania precursor.

According to a preferred aspect of the present invention, it is preferred that the compound having a siloxane bond be formed from the silica precursor have a low refractive index. This feature is advantageous since a film which is not significantly colored and has a high visible light transmittance can be obtained when a transparent substrate is used. Another advantage of the low refractive index is that a small double image can be reduced in the case of a reflector.

(d) Other components

According to a preferred aspect of the present invention, it is preferred that the crystalline titania, the amorphous titania precursor, and the precursor which can be converted to a compound having a siloxane bond above be dispersed in a solvent to form a coating material. Specific examples of the solvent include alcohols such as methanol, ethanol, i-propanol, n-propanol, i-butanol, and n-butanol, and ester compounds such as methyl acetate, ethyl acetate, methyl propionate, and ethyl propionate. When the crystalline titania, the amorphous titania precursor, and the

amorphous titania are dispersed in a solvent in the form of a sol or the like, the solvent may be used as the solvent for other components.

According to another preferred aspect of the present invention, in addition to the above components, the coating material according to the present invention may contain a surfactant, an acid, a hydrolysis catalyst, a polymerization curing catalyst, a leveling agent, an antibacterial metal, a platinum metal, a pH adjuster, or the like.

The addition of the surfactant has such an advantage that the composition according to the present invention can be applied uniformly to the surface of a component. According to a preferred aspect of the present invention, the surfactant is added preferably in an amount of less than 10 parts by weight, and more preferably around 0.1 to 2 parts by weight for one part by weight of the photocatalyst particles. As examples of the surfactant, anionic surfactants such as ammonium salts of polyoxyethylene alkyl phenyl ether sulfonate, sodium salts of polyoxyethylene alkyl phenyl ether sulfonate, fatty acid sodium soaps, fatty acid potash soaps, sodium dioctyl sulfosuccinate, alkyl sulfate, alkyl ether sulfate, soda salts of alkyl sulfate, soda salts of alkyl ether sulfate, polyoxyethylene alkyl ether sulfate, soda salts of polyoxyethylene alkyl ether sulfate, TEA salts of alkyl sulfate, TEA salts of polyoxyethylene alkylether sulfate, sodium salts of 2-ethylhexyl alkyl sulfate, sodium acylmethyltaurate, sodium lauroylmethyltaurate, sodium dodecylbenzenesulfonate, disodium laurylsulfosuccinate, disodium laurylpolyoxyethylene sulfosuccinate, polycarboxylic acid, oleoyl sarcosine, amide ether sulfate, lauroyl sarcosinate, and sodium salts of sulfo FA ester; nonionic surfactants such as polyoxyethylene lauryl ether, polyoxyethylene tridecyl ether, polyoxyethylene cetyl ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene alkyl ether, polyoxyethylene alkyl ester, polyoxyethylene alkyl phenol ether, polyoxyethylene nonylphenyl ether; polyoxyethylene octylphenyl ether, polyoxyethylene laurate, polyoxyethylene stearate, polyoxyethylene alkyl phenyl ether, polyoxyethylene oleate, sorbitan alkyl ester, polyoxyethylene sorbitan alkyl ester,

polyether-modified silicone, polyester-modified silicone, sorbitan laurate, sorbitan stearate, sorbitan palmitate, sorbitan oleate, sorbitan sesquioleate, polyoxyethylene sorbitan laurate, polyoxyethylene sorbitan stearate, polyoxyethylene sorbitan palmitate, polyoxyethylene sorbitan oleate, glycerol stearate, polyglycerol fatty acid ester, alkyl alkyloyl amide, lauric diethanol amide, oleic diethanol amide, oxyethylene dodecylamine, polyoxyethylene dodecylamine, polyoxyethylene alkylamine, polyoxyethylene octadecylamine, polyoxyethylene alkylpropylenediamine, a polyoxyethylene-oxypropylene block polymer, and polyoxyethylene stearate; amphoteric surfactants such as dimethylalkyl betaine, alkyl glycine, amide betaine, and imidazoline; cationic surfactants such as octadecyldimethylbenzylammonium chloride, alkyldimethylbenzylammonium chloride, tetradecyldimethylbenzylammonium chloride, dioleyldimethylammonium chloride, quaternary salts of 1-hydroxyethyl-2-alkylimidazoline, alkylisoquinolium bromide, high molecular amines, octadecyltrimethylammonium chloride, alkyltrimethylammonium chloride, dodecyltrimethylammonium chloride, hexadecyltriethylammonium chloride, behenyltrimethylammonium chloride, quaternary salts of alkyl imidazoline, dialkyl dimethylammonium chloride, octadecylamine acetate, tetradecylamine acetate, alkylpropylenediamine acetate, and didecyldimethylammonium chloride can be given.

According to a preferred aspect of the present invention, the coating material according to the present invention may contain an acid. Due to the addition of the acid, the surface to which the coating material is applied has an increased polarity, and therefore can retain excellent hydrophilicity even in a dark place. Examples of the acid include nitric acid, sulfuric acid, hydrochloric acid, acetic acid, propionic acid, maleic acid, adipic acid, fumaric acid, phthalic acid, valeric acid, butyric acid, citric acid, malic acid, picric acid, formic acid, carbonic acid, and phenol. These acids have a remarkably excellent capability of imparting polarity to the surface. Particularly preferable acids are nitric acid, hydrochloric acid, and sulfuric acid.

According to another preferred aspect of the present invention, the coating material according to the present invention may contain a hydrolysis catalyst for the silica component. The presence of such a catalyst accelerates hydrolysis of an amorphous silica as the precursor. Preferred examples of the catalyst include nitric acid, sulfuric acid, hydrochloric acid, acetic acid, propionic acid, maleic acid, adipic acid, fumaric acid, phthalic acid, valeric acid, butyric acid, citric acid, malic acid, picric acid, formic acid, carbonic acid, and phenol having a pH of 2 to 5.

According to another preferred aspect of the present invention, the coating material according to the present invention may contain a polymerization curing catalyst for a silanol, when the amorphous silica is a silanol. The presence of such a catalyst accelerates the polymerization reaction of the silanol. Preferred examples of the catalyst include aluminum compounds such as an aluminum chelate, aluminum acetylacetonate, aluminum perchloride, aluminium chloride, aluminum isobutoxide, and aluminum isopropoxide; titanium compounds such as tetraisopropyl titanate and tetrabutyl titanate; basic compounds such as lithium hydroxide, sodium hydroxide, potassium hydroxide, sodium methylate, sodium acetate, sodium formate, potassium acetate, potassium formate, potassium propionate, tetramethyl ammonium chloride, and tetramethyl ammonium hydroxide; amine compounds such as n-hexylamine, tributylamine, diazabicycloundecene, ethylenediamine, hexanediamine, diethylenetriamine, tetraethylenepentamine, triethylenetetramine, ethanolamine, gamma-aminopropyltrimethoxysilane, gamma-aminopropylmethyldimethoxysilane, gamma-(2-aminoethyl)-aminopropyltrimethoxysilane, gamma-(2-aminoethyl)-aminopropylmethyldimethoxysilane; tin compounds such as tin acetylacetonate and dibutyl tinooctylate; metal-containing compounds such as cobalt octylate, cobalt acetylacetonate, and iron acetylacetonate; and acid compounds such as phosphoric acid, nitric acid, phthalic acid, p-toluenesulfonic acid, and trichloroacetic acid.

According to a preferred aspect of the present invention, the coating material according to the present invention may contain a leveling agent to form a smooth surface when applied to the surface of a member. The addition of the leveling agent is particularly advantageous when the coating material according to the present invention is applied to a large article. Preferred examples of the leveling agent include diacetone alcohol, ethylene glycol monomethyl ether, 4-hydroxy-4-methyl-2-pentanone, dipropylene glycol, tripropylene glycol, 1-ethoxy-2-propanol, 1-butoxy-2-propanol, propylene glycol monomethyl ether, 1-propoxy-2-propanol, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, and tripropylene glycol monoethyl ether.

According to a preferred aspect of the present invention, the coating material according to the present invention may further contain an antibacterial metal (for example, Ag, Cu, Zn) or a compound thereof. Bacteria which exist on the substrate surface can be killed by adding the above-mentioned metal. Moreover, after the application of the coating material, growth of microorganisms such as a mold, alga, and moss can be suppressed.

According to another aspect of the present invention, the coating material according to the present invention may contain at least one platinum group metal selected from the group consisting of Pt, Pd, Rh, Ru, Os, and Ir. It is known that a surface provided with a photocatalyst formed of a metal compound has stainproof properties, antibacterial properties, and deodorization properties due to the oxidation decomposition activity of the photocatalyst. It is considered that the above activity is maintained on the surface of a member to which the coating material according to the present invention is applied. The above metals are thought to enhance the oxidation decomposition activity of the photocatalyst and improve the antibacterial properties, the deodorization properties, gas decomposition properties, organic-substance decomposition properties and the like of the surface.

The coating material according to the present invention is preferably weakly acidic, neutral, or basic when stored in a tin container or a container provided with a metal lining, or when applied to a metal member. When an acid is added as described above, it is preferable to add a pH adjustor.

The coating material according to the present invention may optionally contain an acid or a base in order to improve the dispersability of solid contents contained therein and to improve storage stability. The coating material may further contain a pigment, a dye, a preservative, and the like.

Production of photocatalytic hydrophilic film

Examples of materials used for the substrate to which the coating material according to the present invention is applied include glass, ceramics, and metals. Various types of glass may be used, such as soda lime glass for construction, quartz glass, alkali-free glass, low thermal expansion glass, and crystallized glass. When using a ceramic substrate, a glazing tile having a glazing layer may preferably be used, for example.

As examples of the substrate explained according to the application, windowpanes for vehicles, windowpanes for buildings, skylights, bay windows, fixed windows, curtain walls, top lights, mirrors such as mirrors for vehicles and bathroom mirrors, cover glass for cameras, sensors, and solar cells, and lighting fittings such as fluorescent lamps and electric bulbs, and the like can be given.

The coating methods according to the present invention may be applied to the substrate using an appropriate method. Preferred coating methods include spray coating, dip coating, flow coating, spin coating, roll coating, brush coating, and sponge coating. The amount of the coating material can be selected appropriately depending on the concentration of the coating material.

After applying the coating material according to the present invention to the

substrate, the substrate is treated under conditions in which the amorphous titania precursor is converted to the crystalline titania, and the precursor which can be converted to a compound having a siloxane bond is converted to a compound having a siloxane bond. It is preferred that the substrate be heated after drying, if necessary. Specifically, simultaneously with the crystallization of the amorphous titania precursor, the compound having a siloxane bond (preferably, amorphous silica or silicone) incorporates crystalline silica, whereby the resulting film adheres to the substrate. Any heating temperature may be used insofar as the coating material can be adhered to the substrate. Generally, the heating temperature is in the range of 20°C to 1000°C. The lower limit is preferably 400°C, and the upper limit is preferably 800°C, and more preferably 600°C.

Generally, it is preferred that heating be performed at a temperature at which the substrate is not deformed. However, heating may be performed such that the coating material adheres to the substrate while deforming the substrate. For example, soda lime glass softens at a temperature exceeding 600°C. When soda lime glass is used as the substrate, it is preferable to heat the substrate at a temperature of 400°C to 600°C. However, when creating a curved mirror, it is possible to heat the substrate at a temperature exceeding 600°C to simultaneously cause the substrate to be thermally deformed. Heat strengthening may be performed at about 800°C to improve impact strength.

A higher heating temperature leads to formation of a film which is dense and has excellent abrasion resistance. Quartz glass can be subjected to heat treatment at a high temperature since quartz glass is not thermally deformed even at a temperature exceeding 600°C. Use of quartz glass as the substrate is advantageous in respect of forming a film which is dense and has excellent abrasion resistance.

According to a preferred aspect of the present invention, when glass, in particular soda lime glass, or a glazing tile is used as the substrate, it is preferred to

provide a sodium diffusion prevention layer on the substrate and apply the coating material to the sodium diffusion prevention layer. Formation of crystalline titania is hindered if sodium ions move from the substrate to the layer of the coating material during heating. This phenomenon can be prevented effectively due to the presence of the sodium diffusion prevention layer. It is preferred that the sodium diffusion prevention layer be formed of silica.

Photocatalytic hydrophilic member

The surface of the substrate to which the coating material according to the present invention is applied and adheres by heating exhibits a high degree of hydrophilicity. This hydrophilicity is considered to be derived from the photocatalytic action of titania. In other words, the photocatalyst exhibits hydrophilicity by photoexcitation. Specifically, when the titania is excited by applying UV rays, water is chemically adsorbed on the surface in the form of a hydroxide group (OH-), whereby the surface becomes super-hydrophilic.

This photocatalytic hydrophilicity is excited by a light source having an energy larger than the band gap of the photocatalyst. Therefore, it is preferred that an anatase-type titania and a rutile-type titania be excited by UV rays having a wavelength of 387 nm or less and 413 nm or less, respectively. As a preferred light source of UV rays, an interior illumination lamp such as a fluorescent lamp, an incandescent lamp, a metal halide lamp, or a mercury lamp may be used. If the substrate is placed outside, the photocatalyst is excited by UV rays contained in sunlight.

The degree of hydrophilicity is preferably 10° or less, preferably about 5° or less, particularly preferably about 0° in terms of the contact angle with water. Generally, when photoexcitation is performed by applying UV rays at an illuminance of 0.001 mW/cm^2 , the substrate surface becomes super-hydrophilic to have a contact angle with water of about 0° within several days. Since the illuminance of UV rays contained in

sunlight is about $0.1-1 \text{ mW/cm}^2$, the substrate surface can be made super-hydrophilic by exposure to sunlight in a shorter period of time. Due to the high degree of hydrophilicity, contaminants adhering to the substrate surface can be readily removed by rinsing with water. In addition, the substrate placed outside has such an advantage that the substrate is self-cleaned by rain water.

Moreover, after the substrate surface to which the coating material according to the present invention is applied has become highly hydrophilic, the hydrophilicity can be retained for a long time even when shaded from light or at night. Further, even if the surface loses hydrophilicity, the surface becomes hydrophilic whenever exposed to sunlight.

EXAMPLES

Preparation of coating liquid

Coating liquid 1

A silicon alkoxide solution (NSi500, manufactured by Nippon Soda Co., Ltd, with a solid component concentration of 5%) for forming an SiO_2 film was diluted with a 1:1 mixture of ethyl acetate and ethanol to have a solid content of 1%.

Coating liquid 2

A titanium alkoxide solution (NTD90, manufactured by Nippon Soda Co., Ltd, with a solid content of 5%) for forming TiO_2 film was diluted with a 1:1 solvent of ethyl acetate and ethanol to a solid content of 0.6%.

Coating liquid 3

A coating material (ST-K01, manufactured by Ishihara Sangyo Co., Ltd, with a solid content of 10%) for forming a TiO_2 film in which a TiO_2 sol and a silicon alkoxide hydrolyzate were mixed at an amount ratio of 80:20 was diluted with a 1:1 solvent of ethyl acetate and ethanol to a solid content of 0.6%.

Coating liquid 4

A coating material (STK-03, manufactured by Ishihara Sangyo Co., Ltd, with a solid content of 10%) for forming a TiO_2 film in which a TiO_2 sol and a silicon alkoxide hydrolyzate were mixed at an amount ratio of 50:50 was diluted with a 1:1 solvent of ethyl acetate and ethanol to a solid content of 0.6%.

Example 1

The coating material was applied by flow coating to form a film. First, an intermediate layer serving as an alkali ion diffusion prevention layer was prepared as follows. The coating liquid 1 was applied to the surface of 2 mm-thick soda lime glass, and dried in a dryer at 120°C for 10 minutes.

The coating liquid 2 and the coating liquid 3 were mixed at a ratio of 90:10. The resulting mixture was stirred to obtain a coating material for forming a hydrophilic film.

The substrate was removed from the dryer and allowed to cool to room temperature. The coating material for forming a hydrophilic film was applied to the substrate by flow coating, and dried in the same manner as mentioned above. Then, the substrate was subjected to heat treatment at 550°C for 30 minutes to obtain a super-hydrophilic film of Example 1.

Examples 2 and 3 and Comparative Example

Super-hydrophilic films of Examples 2 and 3 were obtained in the same manner as in Example 1, except that the mixing ratio of the coating liquid 2 and the coating liquid 3 was changed as shown in the table (given later).

Example 4

A super-hydrophilic film was obtained in the same manner as in Example 1, except that the coating liquid 4 was used instead of the coating liquid 3, and the mixing

ratio of the coating liquid 2 and the coating liquid 4 was set at 70:30.

Performance evaluation test

Evaluation 1: Hydrophilicity evaluation test

Oleic acid was caused to adhere to the surface of a sample. The sample was washed with a neutral detergent and dried. The sample was then irradiated with light from a black light blue lamp (20 W, manufactured by Sankyo Denki) placed 10 cm away from the sample. The contact angle of waterdrops was measured after four hours. The contact angle was evaluated according to the following standard.

A: contact angle was less than 8°

B: contact angle was 8° or more and less than 15°

C: contact angle was 15° or more and less than 25°

D: contact angle was 25° or more

Evaluation 2: Retention of hydrophilicity in dark place

In the same manner as in Evaluation 1, the oleic acid was caused to adhere to the surface of a sample. The sample was washed with a neutral detergent and dried. The sample was then irradiated with light from a black light blue lamp (20 W, manufactured by Sankyo Denki) placed 10 cm away from the sample. After blocking UV rays, the sample was allowed to stand in a shaded state (placed in dark place) for three days. Then, the contact angle was measured. The contact angle was evaluated according to the same standard as in Evaluation 1.

Evaluation 3: Abrasion resistance A sponge brush was moistened with a neutral detergent. The surface of a sample was rubbed vigorously with the brush back and force 20 times. The sample was washed with water and dried. The surface was visually observed for scratches. The results were evaluated according to the following standard.

A: surface was not changed

B: surface was not significantly changed

C: small number of scratches were observed

D: large number of scratches were observed

Evaluation 4: Durability test

The degree of recovery of hydrophilicity of the sample was evaluated every 100 hours by conducting the sunshine weather meter test specified in JIS A-1414. Specifically, the sample was irradiated with light from a black light blue lamp (20 W, manufactured by Sankyo Denki) placed 10 cm away from the sample for one day. The contact angle was then measured. The contact angle was evaluated according to the same standard as in Evaluation 1.

Evaluation 5: Visible light transmittance and haze

The visible light transmittance and haze of the sample were measured using a haze meter manufactured by Gartner Inc.

The results of the above evaluations are summarized in the following table.

	Evaluation 1	Evaluation 2	Evaluation 3	Evaluation 4		Evaluation 5	
				After 100 hrs	After 300 hrs	Visible light transmittance	Haze (%)
Example 1	A	B	A	A	A	80	0.2
Example 2	A	B	A	A	A	83	0.2
Example 3	A	A	A	A	B	85	0.2
Example 4	A	B	A	A	A	84	0.1
Comparative Example	A	D	C	-	-	-	-

CLAIMS

1. A coating material for forming a hydrophilic film comprising at least an amorphous titania precursor, crystalline titania, and a precursor which can be converted to a compound having a siloxane bond.

2. The coating material according to claim 1, wherein the precursor which can be converted to a compound having a siloxane bond is a silica precursor which can form an amorphous silica by heating, its hydrolyzate, its partial hydrolyzate, its hydrolysis-polycondensation product, its partial hydrolysis-polycondensation product, a or a mixture thereof.

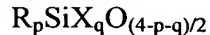
3. The coating material according to claim 1, wherein the amorphous titania precursor is a titanium alkoxide and/or its hydrolyzate.

4. The coating material according to claim 1, wherein the crystalline titania is a sol of titanium oxide.

5. The coating material according to any one of the preceding claims 1 to 3, wherein the silica precursor which can form an amorphous silica by heating is selected from the group consisting of a hydrolyzable silane derivatives expressed by the following general formula,



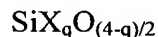
wherein R represents one or more members selected from the group consisting of a hydrogen atom and an organic group, X represents one or more members selected from the group consisting of an alkoxy group and a halogen atom, and p represents 1 or 2, a siloxane represented by the following compositional formula,



wherein R is as defined above, X represents one or more members selected from the group consisting of an alkoxy group and a halogen atom, p represents a number satisfying $0 < p < 2$, and q represents a number satisfying $0 < q < 4$, a tetrafunctional hydrolyzable silane compound represented by the following general formula,



wherein X represents one or more members selected from the group consisting of an alkoxy group, and a silicate represented by the following average compositional formula,



wherein X represents one or more members selected from the group consisting of an alkoxy group and a halogen atom, and q is a number satisfying $0 < q < 4$.

6. The coating material according to any one of the preceding claims 1 to 5, wherein the amount of the crystalline titania accounts for 6 to 45 wt% of the total amount of a titanium oxide.

7. The coating material according to any one of the preceding claims 1 to 6, wherein the amount of the crystalline titania accounts for 60 to 40 wt% of the total solid content of the coating material.

8. The coating material according to any of claims 1 to 7, wherein the converted weight of SiO_2 in the precursor which can be converted to a compound having a siloxane bond is preferably 50% or less of the converted weight of TiO_2 in the amorphous titania precursor.

9. A method of forming a photocatalytic film comprising applying the coating

material according to any one of the preceding claims 1 to 8 to a substrate and allowing the coating material to adhere to the surface of the substrate.

10. The method of forming a photocatalytic film according to claim 9, wherein the coating material is allowed to adhere to the substrate by heating.

11. The method of forming a photocatalytic film according to claim 10, wherein the heating is performed by subjecting the substrate surface to a heat treatment at a temperature of 400°C to 800°C.

12. The method of forming a photocatalytic film according to any one of the preceding claims 9 to 11, wherein the substrate is glass.

13. The method of forming a photocatalytic film according to claim 12, wherein a sodium diffusion prevention layer is provided on the substrate and the coating material is applied thereon.

14. A photocatalytic hydrophilic member obtained by the method according to any one of the preceding claims 9 to 13. ,

ABSTRACT

A coating material capable of forming a hydrophilic film which is satisfactory in durability, hardness, transparency, and visible light transmittance and retains hydrophilicity for a long time even when shaded from light. This coating material comprises at least an amorphous titania precursor, crystalline titania, and a precursor which can be converted to a compound having a siloxane bond.